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Kinetics and Reaction Mechanism of Hydrolysis of N-Salicylidene-*m*-Methyl Aniline Spectrophotometrically

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The kinetic study of the hydrolysis of the Schiff base, N-salicylidene -*m*-methyl aniline (HL) has been done in the pH range 3.57–12.65 in the temperature range 29°–45°C. A rate profile diagram of pH vs. rate constant shows a rate minimum in the pH range 5.42–9.95 and the rate is practically constant at pH > 10.76. Suitable reaction mechanisms have been suggested for the hydrolysis of the Schiff base in acidic, neutral and basic media. From the effect of temperature on the reaction rate, the various thermodynamic parameters have been calculated.

INTRODUCTION

The kinetic study of the formation and hydrolysis of imines is important due to its close relation to the conversion of > C=O= to >C=N and vice versa in biochemical processes.[1–4] The effect of hydrogen ions, hydroxyl ions and metal ions on the hydrolysis of some imines has been studied[4–11]. In this paper we are reporting the kinetics and the reaction mechanism of the hydrolysis of N-salicylidene-*m*-methyl aniline in acidic, neutral and basic media.

EXPERIMENTAL

The imine was prepared by refluxing a mixture of salicylaldehyde and *m*-toluidine in ethanolic medium for about an hr. The solution was cooled to obtain yellow-coloured crystals of the Schiff base. The crystals were separated and recrystallised from ethanol, m.pt. 48°C. The structure was confirmed by elemental analysis and i.r. spectra.

(Found: C, 79.60; H, 6.20; N, 6.62; O, 7.54%. Calc: C, 79.62; H, 6.16; N, 6.63; O, 7.58%)

$\bar{\nu}_{max}$(KBr) 1615 cm^{-1} (ν_{C-N}), 1360 cm^{-1} (δ_{CH} of $-CH_3$ group) and 3200–2500 cm^{-1} (ν_{OH}.)

Kinetic Measurements

The hydrolysis of the imine was studied spectrophotometrically in a series of universal buffer solutions in the pH range 3.57–12.65°C in 40% ethanol-water (v/v) medium in the temperature range 29–45°C. The pH values of the buffers used were determined using an "ELICO LI–120" digital pH meter. The concentration of the imine was kept at 4×10^{-4} mol. dm^{-3}. The ionic strength of the reaction mixture was maintained at $\mu = 0.1$ mol. dm^{-3} using 1 M sodium perchlorate (E. Merck). All other chemicals used were of AR grade (E. Merck).

A solution of sodium perchlorate, buffer and absolute ethanol in required amounts was allowed to equilibrate in a previously adjusted thermostat (accuracy ± 0.1°). The reaction was initiated by adding a known volume of the stock solution of the imine in ethanol which was also maintained at the same temperature. The progress of the reaction was followed by measuring the decrease of absorbance of the imine with time at $\lambda = 400$ nm using "ELICO Ultra Spec Model CL-54" spectrophotometer.

The plots of log $(A_t - A_\infty)$ against time were found to be straight lines and the pseudo first order rate constants were calculated from the slopes of these plots. From the effect of temperature on the reaction rate, the energy of activation (E) and other thermodynamic parameters were evaluated.

Equilibrium Constants

The equilibria involving the imine (HL) may be represented as

$$H_2L^+ \overset{K_1}{\rightleftarrows} HL + H^+ \qquad (1)$$

$$HL \overset{K_1}{\rightleftarrows} L^- + H^+ \qquad (2)$$

where H_2L^+, HL and L^- stand for its protonated, neutral and anionic (due to deprotonation of the phenolic group) forms respectively.

pK_1 was determined by a potentiometric titration of 4×10^{-4} M imine against 0.1 M HCl using a digital pH meter, equipped with a combined glass-calomel electrode assembly.

pK_1 was found to be 4.498 in 40% ethanol-water (v/v) medium at 29°C and $\mu = 0.1$ mol. dm^{-3}.

The Schiff base anion (L^-) shows an absorption maximum at $\lambda = 400$ nm. pK_2 was calculated spectrophotometrically as 9.712 in 40% ethanol-water (v/v) medium at 29°C and $\mu = 0.1$ mol. dm^{-3}.

RESULTS AND DISCUSSIONS

The rate constants in the pH range 3.57–12.65 at 29°C are listed in Table 1. A rate profile diagram of pH vs. rate constant at 29°C and $\mu = 0.1$ mol. dm^{-3} shows the rate minimum at $7.04 < \text{pH} < 10.76$ and the rate is almost constant at $\text{pH} > 10.76$ (Fig. 1).

Rate-limiting Pathways

In the pH range 3.57–12.65, the imine (HL) may be assumed to undergo hydrolysis by four rate-determining pathways.[9].

(i) an acid-catalysed addition of water to the imine linkage of the protonated imine, H_2L^+ (k_1).

(ii) a spontaneous addition of water to the imine linkage of neutral imine, HL (K_2).

(iii) the addition of water to the imine anion, L^- (k_3).

(iv) the addition of hydroxyl ion to the imine anion, L^- (k_4).

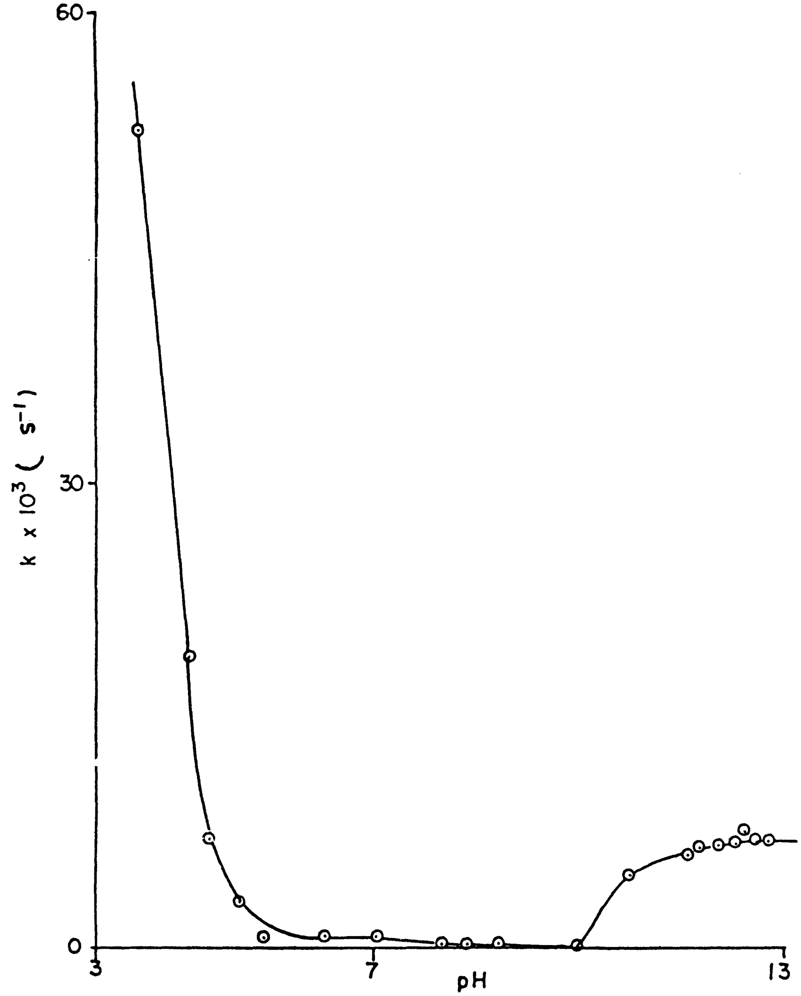

Fig. 1. Plot of $k \times 10^3$ (s^{-1}) against pH at 29°C for the hydrolysis of N-salicylidene-*m*-methylaniline [B] at $\mu = 0.1$ mol-dm^{-3}

Step 4 in which hydroxyl ion predominates may be eliminated as the rate constant was found to be almost independent of the hydroxyl ion concentration at pH > 10.76 (Table 1).

Thus the overall rate of hydrolysis will be

$$\text{Rate} = k_1(H_2L^+) + k_2(HL) + k_3(L^-) \quad (3)$$

Hydrolysis of Schiff base in acidic and neutral ranges of pH

The rate constant varies linearly with hydrogen ion concentration in the pH range 4.36–7.04 (Table 1). In this acidic pH range, equation (3) reduces to

$$\text{Rate} = k_1(H_2L^+) + k_2(HL)$$

$$k = \frac{k_1}{K_1}(H^+) + k_2 \quad (4)$$

TABLE 1
RATE CONSTANT DATA FOR THE HYDROLYSIS OF N-SALICYLIDENE-*m*-METHYL ANILINE
Ethanol-Water = 40% (v/v), Temp. = 29°C, $\mu = 0.1$ mol dm^{-3}

pH	$(H^+) \times 10^7$ mol dm^{-3}	$(OH^-) \times 10^3$ mol dm^{-3}	$k \times 10^3$ s^{-1}
3.57	2692.00	–	52.64
4.36	436.50	–	19.00
4.58	263.00	–	7.24
5.06	87.10	–	3.00
5.42	38.02	–	0.50
6.30	5.01	–	0.53
7.04	0.91	–	0.56
10.76	–	0.58	4.80
11.60	–	3.98	6.00
11.75	–	5.62	6.40
12.00	–	10.00	6.45
12.30	–	19.95	6.75
12.39	–	24.55	7.41
12.60	–	39.81	6.90
12.65	–	44.67	6.91

A plot of k vs. (H^+) is a straight line (Fig. 2) with a slope of k_1/K_1 from which k_1, the rate constant for the addition of water to the protonated imine, can be calculated.

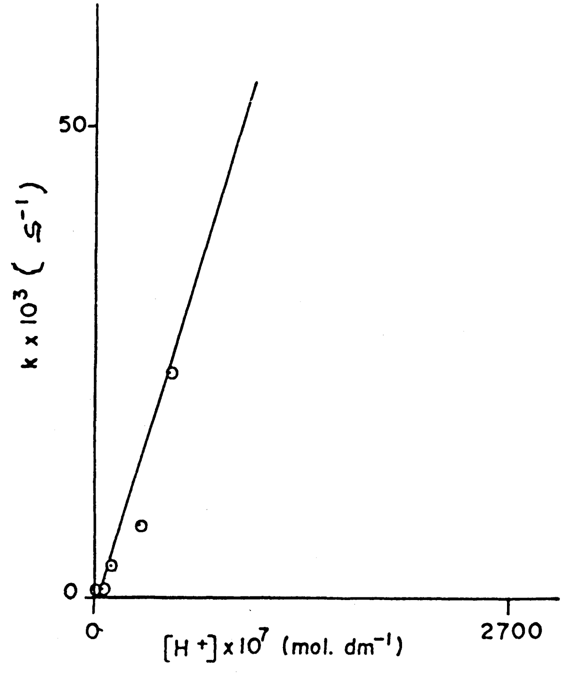

Fig. 2 Plot of $k \times 10^3$ (s^{-1}) against $[H^+] \times 10^7$ (mol. dm^{-3}) for N-salicylidene-*m*-methylaniline at $\mu = 0.1$ mol. dm^{-3}

$$k_1 = 16.01 \times 10^{-3}\ s^{-1} \text{ at } 29°C.$$

As the intercept of the plot is zero, k_2 is taken as zero. The rate constant for pH = 3.57 does not fall on the straight line ($pK_1 = 4.498$). This may be due to the fact that the imine is not appreciably protonated at pH < 4.36 and suggests that the acid catalysis involves only the conversion of the imine to its conjugate acid in a rapid pre-equilibrium followed by the slow attack of water.

Chart I outlines the reaction mechanism of the acid-catalysed hydrolysis of the

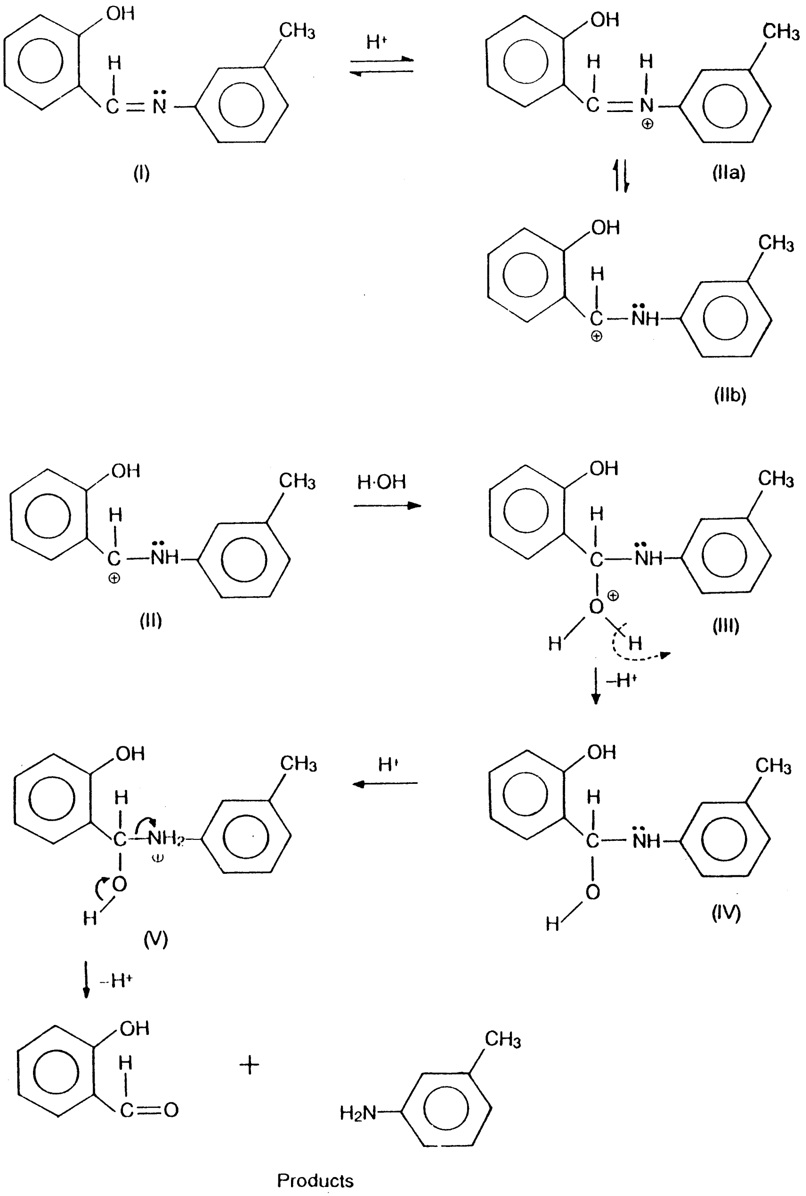

Chart I

imine. The rate-determining step suggested is the proton-catalysed attack of water at the reactive imine linkage of HL.

In the neutral range pH 5.42 to 7.04 the rate is minimum and almost constant. The negligible rates are due to very low catalytic activity of proton in the neutral pH range as a result of which the protonation of the imine is negligible. Consequently the attack of water on the protonated Schiff base is very slow. The addition of water to neutral imine[10] (HL) is therefore suggested as rate-limiting step.

In the hydrolysis study specific acid catalysis is assumed, as no general catalysis was observed (Table 2).

TABLE 2
GENERAL ACID-BASE CATALYSIS FOR THE HYDROLYSIS OF N-SALICYLIDENE-*m*-METHYL ANILINE
Ethanol-Water = 40% (v/v), Temp. = 29°C, μ = 0.1 mol.dm^{-3}

Potassium hydrogen phthalate (PHP) and hydrochloric acid buffer (pH = 3.57)					
([PHP] + [HCl]) × 10^3 (mol dm^{-3})	2.25	4.50	6.75	9.00	11.25
k × 10^3 (s^{-1})	47.30	46.06	46.06	49.90	52.60
Acetate Buffer (pH = 4.58)					
([HA) + [A$^-$]) × 10^3 (mol dm^{-3})	8.00	16.00	24.00	32.00	40.00
k × 10^3 (s^{-1})	8.35	9.35	8.09	8.44	8.62
Phosphate Buffer (pH = 7.04)					
([$H_2PO_4^-$] + [HPO_4^{-2}]) × 10^3 (mol dm^{-3})	8.00	16.00	24.00	32.00	40.00
k × 10^3 (s^{-1})	0.51	0.53	0.54	0.49	0.56
Carbonate Buffer (pH = 10.76)					
([HCO_3^-] + [CO_3^{-2}] × 10^3 (mol dm^{-3})	4.00	8.00	12.00	16.00	20.00
k × 10^3 (s^{-1})	3.80	3.61	3.50	3.73	4.40

Hydrolysis of Schiff base in basic medium

In the basic range pH > 9.95, the rate constant initially increases with increase in pH and is nearly independent of hydroxyl ion concentration at pH > 10.76 (Table 1). In this pH range, the imine may be assumed to be exclusively in the anionic form L$^-$ (pk_2 = 9.712) due to the neutralisation of the phenolic proton of the *ortho*-hydroxyl group by the OH$^-$ ion of alkali[9]. The above observations lead to the assumption that the complex formed may be "Arrhenius Complex". In the presence of excess catalyst, "Arrhenius Complex" leads to "specific hydroxyl ion catalysis" at low hydroxyl ion concentration and the rate reaches a limiting value at high hydroxyl ion concentration[13]. In the present study it is found that the rate increases with the hydroxyl ion concentration at low hydroxyl ion concentration. Since no general catalysis was observed in this region (Table 2), specific hydroxyl ion catalysis may be assumed. Further the rate reaches a limiting value at higher hydroxyl ion concentrations. All these facts indicate that the rate-limiting step is the slow reaction of water with the imine anion L$^-$ (k_4)[9,13] (Chart II). The average value of the rate constants at pH > 10.76 is taken as k_4.

$$(k_4 = 6.69 \times 10^{-3}\ S^{-1} \text{ at } 29°C)$$

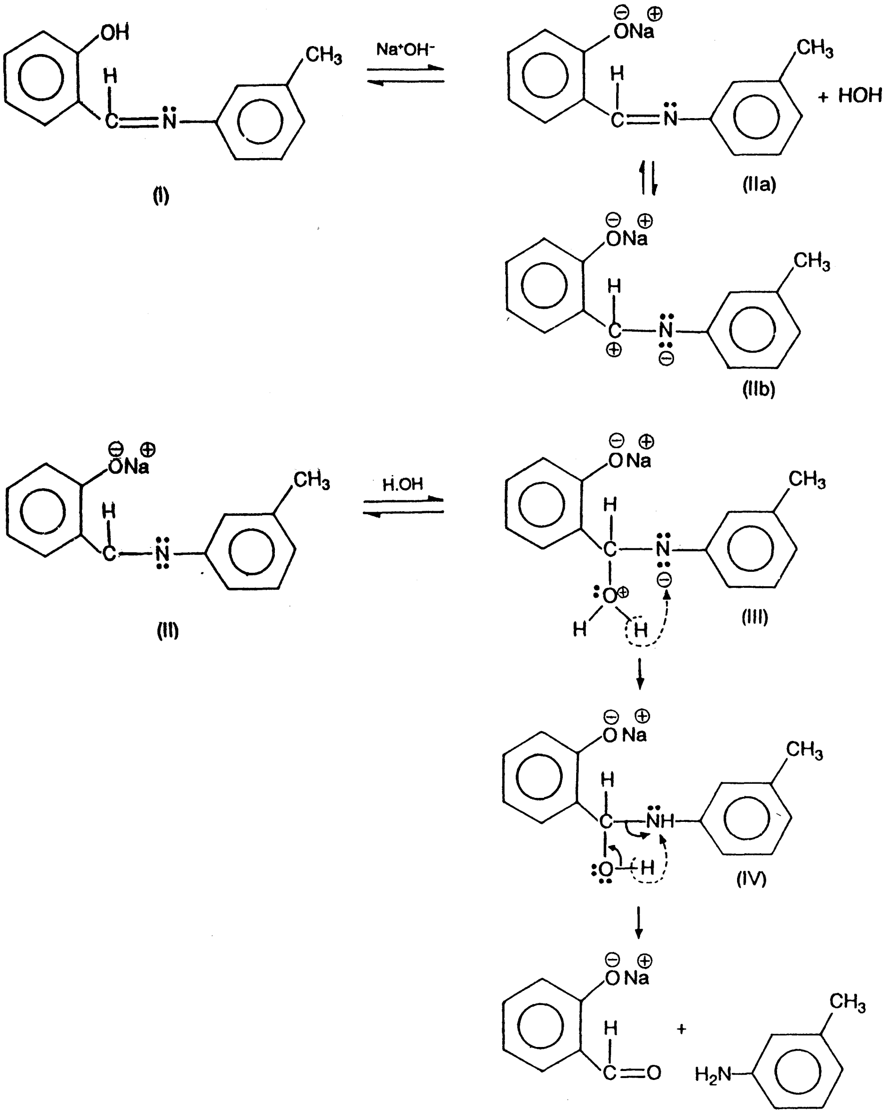

Chart II

Effect of Temperature and Thermodynamic Parameters

The hydrolysis of the imine was studied in the temperature range 29–45°C. From the effect of temperature on the reaction rate, the various thermodynamic parameters like energy of activation (E), probability factor (PZ), ΔH^*, ΔG^* and ΔS^* were calculated. ΔS^* values range from $-62.83\ JK^{-1}\ mol^{-1}$ to $-233.74\ JK^{-1}\ mol^{-1}$ in the pH range 3.57–12.65.

The negative activation entropies can perhaps be explained by a model in which the water molecules are tightly held to the imine linkage, the nucleus of the hydrolytic reaction. The large negative values of ΔS^* may indicate and extensive re-orientation of solvent molecules as a result of the formation of the activated complex[5].

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